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In re Patent Application of

Vuorinen et al   Atty. Ref.:   30-336

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For: METHOD OF TREATING CELLULOSIC PULP

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November 5, 1997

Honorable Commissioner of Patents
 and Trademarks
Washington, DC 20231

SUBMISSION OF ADDITIONAL INFORMATION

Sir:

Enclosed herewith is an article published in the October, 1977 issue of Pulp &
Paper Magazine which describes the significance of hexenuronic acids and their affects
on bleaching as well as methods for removing them. This is another indication of the
clear unobviousness of the invention since it is an article by another (even though the
assignee has a cooperation agreement in place with the authors' employer -- Solvay
Interox) which clearly supports all of the arguments earlier made by applicant regarding
the advantages and the unobviousness of the invention.

Since another evidentiary declaration will be submitted it is requested that action
be held in abeyance in this case for a further period of time.

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Strategy for better managing transition metals prevents costly side reactions with H_2O_2 and makes pressurized oxygen stages more efficient

BY J.R. PRESLEY, R.T. HILL, E. CHAUVEHEID, and J. DEVENYNS

New Metals Control Technique Improves Bleaching Performance

A S KRAFT PULP MILLS MOVE TOWARD "minimum impact" manufacturing, one of the most difficult challenges is the development of strategies for dealing effectively with buildup, carryover, and recovery of organic and inorganic residues. Large volumes of acidic, chloride-containing bleach plant filtrates are prohibitive to mill closure because of their incompatibility with the kraft recovery process. As a result, chloride-containing filtrate streams are minimized to improve the potential degree of closure, making recovery or separate treatment of the problematic effluents affordable.

Minimum impact practices rely heavily on the use of hydrogen peroxide, irrespective of whether a mill's process is elemental chlorine free (ECF) or totally chlorine free (TCF). With pressurized peroxide stages cost-effectively substituting for ClO_2, a significant reduction in both organic and inorganic chloride levels, required for effective bleach plant filtrate recovery, can be achieved.

Metals control is the key issue in assuring optimal performance from hydrogen peroxide-based delignifying and bleaching stages. And as mills increase their level of filtrate recovery, there can be a buildup of transition metals in the process waters, reducing the effectiveness of hydrogen peroxide.

This article details the results of a study that concentrated on improving the operational flexibility of metals control prior to peroxide bleaching. This new strategy for metals control leads to better performance in pressurized oxygen (PO) stages, as well as greater flexibility in counter-current filtrate recovery.

PULP CHELATION PROPERTIES. The removal of detrimental metals from kraft pulps has been an active field of research for several years. It is well established that kraft pulps possess metal ion binding sites and that external synthetic chelants are needed to compete for these metals. Under alkaline pH conditions, where aminocarboxylates reach their highest affinity for dissolved transition metals, kraft pulp apparently has an even stronger chelating affinity, indicated by experimental evidence, and therefore wins the competition for transition metals. As a consequence, metals control with aminocarboxylate chelants is only efficient in a pH range from slightly acid to neutral.[1,2]

Previous investigation of the chelation pH profile of pulps[3] showed that chemical pulps behave differently from mechanical pulps with respect to metals binding. For chemical pulps, the pH profile for efficient metals control is narrow compared with that for mechanical pulps. Despite these early efforts, a complete and comprehensive understanding was still lacking. We postulated that the chemical nature of uronic acids in both types of pulps could explain their different chelation properties (Figure 1).

In 1995, breakthrough research in carbohydrate chemistry shed new light on the precise chemical nature of uronic acids in chemical pulps. The work, reported from Finnish research groups[4], identified hexenuronic acids as a uronic acids subclass, formed under alkaline cooking processes. These new findings are at the base of observed differences in chelation profile of (chemical) kraft pulps and mechanical pulps. There are strong indications that in mechanical pulps, the uronic acids involved in metals retention are those of the native wood (mainly the 4-O-methyl-

FIGURE 1: Brightness after peroxide bleaching in relation to the chelation pH profile for chemical (CHP) and mechanical (HYP) pulps.
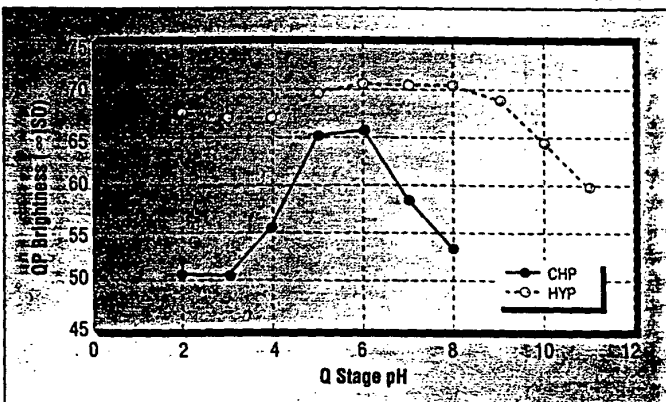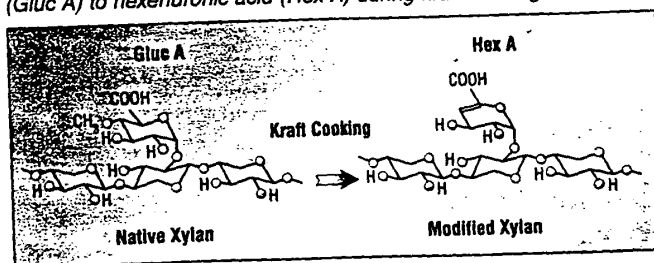
FIGURE 2: Chemical transformation of 4-O-methylglucuronic acid (Gluc A) to hexenuronic acid (Hex A) during kraft cooking.

complete removal of hexenuronic acids at pH 3. The major peculiarity of this acid stage is its temperature—the temperature should be higher than 80°C to ensure nearly complete hydrolysis of the hexenuronic acids. This "hot acid" stage is represented by "A*" to stress its drastic temperature conditions.

Due to their chemical nature, the hexenuronic acids are hydrolyzed faster than all other sugar oligomers and polymers. This facilitates a selective hydrolysis reaction without a significant yield loss.

glucuronic acid side group of the xylan polymers). In kraft pulps, on the other hand, the uronic acids involved in metals retention are hexenuronic acids, transformed from their native uronic acid precursors during the kraft cooking process (Figure 2).
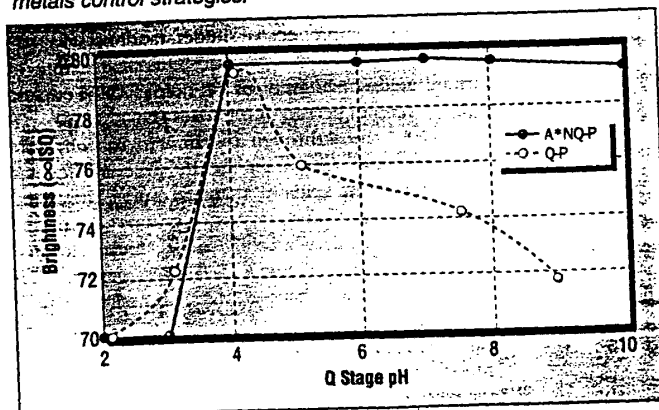
Our previous research work indicated that hexenuronic acids have a higher affinity for transition metals than their 4-O-methylglucuronic acid precursors. Therefore, the destruction or removal of hexenuronic acids from kraft pulp will reduce the pulp's chelating affinity, and hence facilitate desorption of transition metals. These basic concepts on metal extraction from kraft pulps constitute the foundation of our new strategy for metals control.

THE NEW STRATEGY. The new strategy for metals control tackles the transition metals problem at the root. It is based on processes that destroy the sites on the pulp fibers where transition metals are attached. As a result, it can be considered a cure and not a remedy.

Hexenuronic acid groups can be destroyed effectively by acid-oxidative treatments or by hot acid hydrolysis. Due to the acidic reaction conditions in these treatments, a large part of the beneficial metals, such as magnesium, are ion exchanged from the pulp. To avoid leaching these beneficial metals, a redeposition step for alkaline-earth metals should follow acid hexenuronic acid treatment prior to any washing operation. This can be achieved by means of a pH adjustment of the pulp slurry, which is called neutralization. The selective removal of the detrimental metals can then proceed using a chelation stage employing conventional chelants. The new strategy for metals control can be summarized in the following sequence: A*NQ where A* stands for the hot acid stage, N for the neutralization or redeposition of the beneficial metals, and Q for the chelation stage. The N step is not necessarily a separate stage, since there is no intermediate washing, and the N treatment requires no more than a dosing point where pH can be raised. Washing in between the A*N and Q treatments is optional.

Following this metals control sub-sequence, the pulp is washed to remove the chelated detrimental metals. The hydrogen peroxide stage, included in a TCF or ECF bleaching line, can then proceed.

EFFECT OF CHELATION AND PEROXIDE BLEACHING. The removal of hexenuronic acids from the kraft pulps leads to an unprecedented consequence for chelation. The chelation profile of a chemical (kraft) pulp is significantly broadened, raising the pH range for efficient metal chelation dramatically from an alkaline endpoint of pH 7 to an alkaline endpoint of pH 10.

This new observation can be illustrated through the brightness response after hydrogen peroxide bleaching as a function of the pH of the chelation stage. When the metals control strategy is applied before the hydrogen peroxide bleaching stage—for a chelation pH range between 4 and 10—the pulp brightness will remain the same after bleaching. This is not the case for a conventional Q-P sequence. This effect was reproduced for hardwoods, softwoods, and eucalyptus kraft pulps.

The enlargement of the chelation pH profile when hexenuronic acids are removed from kraft pulps explains the difference between chelation profiles of

The new strategy for metals control leads to better performance in pressurized (PO)-stages, as well as greater flexibility in countercurrent filtrate recovery.

REMOVING HEXENURONIC ACIDS. The removal of hexenuronic acids is an important step for improving the metals control. A selective acid hydrolysis has been described by Finnish research groups[5], resulting in a

FIGURE 3: Brightness after peroxide bleaching in relation to the chelation pH profile for the new (A*NQ) and conventional (Q-P) metals control strategies.

chemical and mechanical pulps. Hexenuronic acids, which are not formed under mechanical pulp processing, are stronger pulp chelant groups than the native 4-O-methylglucuronic acid. At pH higher than 6-7, the hexenuronic acids of a conventional kraft pulp become stronger than the organic chelants introduced in the chelation stage. When these strong (kraft pulp) chelants are removed, the chelation behavior of kraft pulp is similar to mechanical pulp, since the uronic acids remaining are the same for both pulps.

The chelation of a kraft pulp can be performed—and more importantly finished—under highly alkaline conditions. This should give more flexibility to the bleach plant process, since careful follow-up of the chelation pH is no longer needed. This follows from the improved control of detrimental metals before the hydrogen peroxide bleaching stage. The increased stability of hydrogen peroxide allows higher, more aggressive temperatures (beyond conventional bleaching conditions) in pressurized bleaching towers with confidence. These developments should make hydrogen peroxide an even more reliable bleaching chemical for kraft chemical pulp processing.

APPLYING THE STRATEGY TO KRAFT PULPS.
For ECF bleaching lines, a key challenge in mill closure is reduction of the amount of organic and inorganic chlorides. Partial replacement of ClO_2 with hydrogen peroxide can reduce the chloride problem in the bleach plant effluent. The new strategy for metals control offers an improved efficiency of the hydrogen peroxide bleaching stage.

Beginning from the conventional ECF bleaching sequence, D0-E-D1-E-D2, a peroxide stage can be introduced either prior to, or following the sequence, in place of D0-E or D1-E, respectively. Where should this metals control strategy be implemented in the bleach-

FIGURE 4: Conditional stability constants of manganese for aminocarboxylate chelants and for pulps with and without hexenuronic acid.
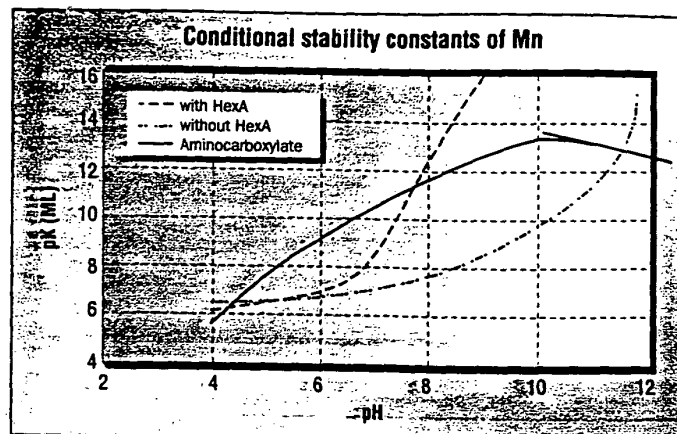
can be removed efficiently at the early stage of the bleaching sequence.

Some other benefits from this A*NQ-P-D-E-D sequence can be obtained from the removal of the D0 stage. Previous research on ECF sequences[6], has shown that replacing ClO_2 with hydrogen peroxide can reduce ClO_2 demand by 40%. In light of the effect of such a replacement on AOX measurements, it is clearly advantageous to start the sequence with hydrogen peroxide delignification, since it reduces the kappa number prior to the application of chlorine dioxide. As previously noted, the reduction in chlorinated organic compounds might facilitate "closing up" the filtrate loops. While more COD is created with hydrogen peroxide delignification, these organic compounds have positive fuel value when burned in the recovery boiler.

In 1995, breakthrough research in carbohydrate chemistry shed new light on the precise chemical nature of uronic acids in chemical pulps.

ing sequence? Several cases for partial replacement of ClO_2 with hydrogen peroxide have been considered.

Case 1: At the beginning of the ECF sequence. For a Q-P-D-E-D bleaching sequence, the answer to the question is quite obvious: The hot acid stage should be introduced just before the chelation stage. The sequence would then be A*NQ-P-D-E-D. As has been shown previously, the chelation step can be operated under alkaline conditions, which means that the acid effluent from the hot acid stage is neutralized or becomes alkaline during the neutralization step.

As a result, the effluent from the Q stage, which will not be charged with chlorinated organics, can be processed through the kraft recovery cycle. Further, recycling the alkaline effluent from the hydrogen peroxide stage, either completely or partially, can aid in neutralizing the pulp at the end of the hot acid stage. With this bleaching configuration, transition metals

Case 2: At the end of the ECF sequence. The removal of hexenuronic acids should be done in the early stage of the D-E-D-Q-P bleaching sequence. Since hexenuronic acid groups contribute to kappa number and consume oxidizing chemicals, early removal will reduce the amount of ClO_2 that would then be needed in the first D stage, allowing some further oxidant savings and less chlorinated organic compounds. Moreover, the hot acid stage and the first chlorine dioxide stage can be operated without intermediate washing in a A*D-E-D-NQ-P bleaching sequence[7]. Treatments with ClO_2 may further reduce the quantities of residual hexenuronic acids. Prior to metals chelation, the pH of the pulp should be adjusted to an alkaline level, permitting recycling of alkaline Q stage effluent to the kraft recovery cycle.

In bleaching eucalyptus to full brightness with a D0-E-D1-Q-P sequence, the kappa number after the

FIGURE 5: *Hydrogen peroxide consumption after bleaching, in relation to the chelation pH profile for the new (A*NQ) and conventional (Q-P) metals control strategies.*
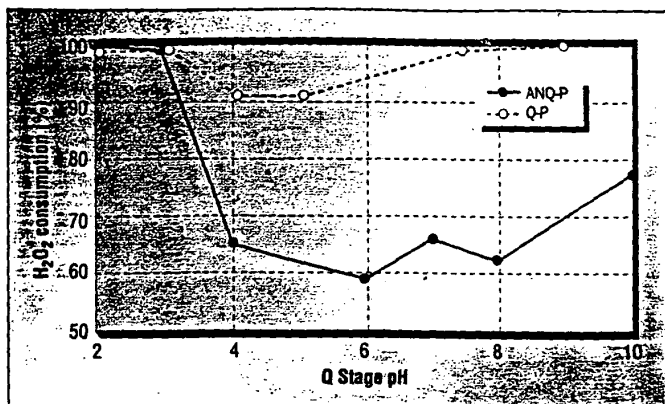
D1 stage decreased from 10 to 4 units with 0.9% ClO_2 in both D stages. When a Hot Acid hydrolyses was introduced at the beginning of the sequence, the same kappa drop was observed after the A*-D0 stages, suggesting the potential for ClO_2 savings in the bleach plant. This can be attributed to the removal of the hexenuronic acids, which contributes to the kappa number or oxidant consumption.

Case 3: At the beginning and the end of the ECF sequence. A few years ago, hydrogen peroxide introduced at the beginning and at the end of an ECF bleaching sequence was recommended for kraft pulp delignification, but the detrimental metals had to be removed to assure efficiency. It was reported[8] that an acid stage operated at 60°C to 80°C could improve the delignification potential of hydrogen peroxide, but no particular attention was dedicated to the impact of the stage on metal profile.

With such an acid treatment before the hydrogen peroxide delignification stage, it was shown that kraft pulps could be bleached with an A-P-D-P sequence (containing hydrogen peroxide delignification and brightening stages) to a same extent as with a C-E-D-E-D bleaching sequence. At that time, the kappa drop was attributed to the breakdown of some alkali resistant lignin bonding (ether bonds). The more recent research suggests that the destruction (oxidation) of hexenuronic acids seems a more appropriate explanation.

With the hot acid strategy for metals control, the delignification and brightening potential of hydrogen peroxide for kraft pulps can be improved, making an A*NQ-P-D-P sequence feasible. Whether a second chelation stage (before the hydrogen peroxide brightening stage) would be needed depends on the initial metal profile of the pulp and on the efficiency of the first chelation stage. Again, the removal of hexenuronic acids would allow the operation of both chelation stages under alkaline conditions, facilitating the recycling of the Q effluents to the kraft recovery cycle. This bleaching configuration would reduce tremendously the volume of acid filtrate generated and the amount of organic and inorganic chloride in the bleach plant effluents.

The industrial application of hydrogen peroxide at both the beginning and the end of the ECF sequence has been hindered in the past because of the large quantities required by high kappa number of kraft pulps. With the development of extended kraft cooking and oxygen delignification (which in combination can reduce kappa numbers by 20 units), and with the availability and improved efficiency of hydrogen peroxide, kraft mills could reconsider peroxide delignification and brightening.

Now, more and more ECF bleaching sequences are preceded by an oxygen delignification stage to augment the lignin removal obtained from kraft cooking. Both configurations–O-A* and A*-O–should be considered because no significant differences in pulp characteristics, such as kappa number, viscosity, and yield have been noticed[5].

Running the chelation stage under alkaline conditions also allows combining it with an oxygen stage and favors the A*NOQ delignification configuration before further use of hydrogen peroxide in the bleach plant, instead of the reverse option.

OTHER ADVANTAGES. Several other advantages of a Hot Acid stage for hydrogen peroxide bleaching have been described elsewhere.[5] As previously discussed, hexenuronic acids contribute significantly to the kappa number of kraft pulps. This is due to their double carbon-carbon bond, which contributes to the oxidant consumption in the bleach plant. Hexenuronic acids are destroyed by acid-oxidant chemicals such as chlorine, chlorine dioxide, ozone, or peracids. If hexenuronic acids are removed from the pulp with a non-oxidant stage, such as the hot acid stage, the consumption of these acid-oxidant chemicals will decrease.

The removal of hexenuronic acids from the kraft pulps leads to an unprecedented consequence for the chelation

Conversely, oxidant chemicals such as alkaline hydrogen peroxide and oxygen are unable to remove the hexenuronic acids from kraft pulps. The lower consumption of acid oxidant chemicals should be significant for hardwoods, which contain more hexenuronic acid groups than softwoods. For eucalyptus, important kappa drops have been observed after the hot acid stage, reflecting large amounts of hexenuronic acids.

When hexenuronic acids are oxidized, their conjugated double carbon-carbon bond is disrupted and oxalic acid or oxalate is generated. This degradation product represents a nightmare for facilities working towards mill closure, due to its well-know scaling properties with calcium cations.[9] Currently, hexenuronic acids are considered a major source of oxalate in the pulp mill.[5] With the use of the hot acid stage, the hexenuronic acids are removed without dis-

ruption of their double bond. The formation of oxalate is avoided. The hot acid stage could reduce existing or potential scaling problems, simplifying the minimum impact manufacturing issue for kraft mills.

One last consequence resulting from the presence of hexenuronic acids is related to the brightness reversion of kraft pulps. The conjugated double carbon-carbon bond in the hexenuronic acid promotes chromophore formation under aging conditions. Consequently, the removal of the hexenuronic acids from kraft pulps will improve the brightness stability of the bleached pulp.

With ECF bleached pulps, the benefit is small since a large part of the hexenuronic acids formed are removed by successive chlorine dioxide delignification and bleaching stages. But for TCF pulps, the use of oxygen and hydrogen peroxide could leave a larger amount of hexenuronic acids. The replacement of chlorine dioxide with hydrogen peroxide in ECF bleaching could lead to an increase in the amount of hexenuronic acids in the bleached pulps. The application of the hot acid stage will decrease the brightness reversion tendency of kraft pulps. ∎

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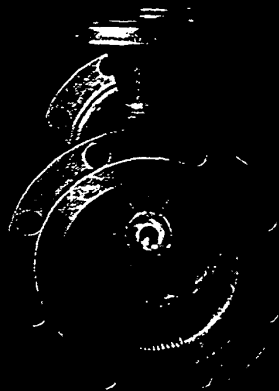
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